

Laboratory Cracking Data as a Basis for Plant Design

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Laboratory Cracking Data as a Basis for Plant Design

 IN THE design of cracking plants, the petroleum refining industry has come to realize the necessity of developing scientific methods in order to replace the empiricism of the past. This trend has been evidenced by an increased interest both in the pyrolysis of certain relatively pure compounds and also by the building of pilot cracking plants for the purpose of obtaining data on commercial charging stocks. The designer is interested primarily in the rates of formation of gas, gasoline, tar, and coke as influenced by the variables time, temperature, and pressure. Both the bomb (static method) (15, 18) and the pilot plant (flow process) (6, 7, 13, 19) have been used in obtaining these quantitative laboratory data. Although the pilot plant may be an exact duplication of a large-scale plant, data secured from such apparatus, especially one which is operating under high pressure, do not provide the investigator with the densities of the charge from time to

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time during the cracking operation. Without this information, the calculation of cracking rates and the design of continuous plants are largely a matter of guesswork. This investigation was undertaken, therefore, to develop a laboratory method of measuring the actual densities of the charge during the cracking period, so that the elapsed time at certain cracking temperatures might be measured directly.

Experimental Work

APPARATUS. The apparatus used in this work consisted of two bombs machined out of bars of S. A. E. 1020 low-carbon steel, with the necessary heating bath, transfer lines, and valves. Figure 1 shows a cross-sectional view of the bombs and special high-pressure fittings. These cone and cap screw fittings are similar to those designed by the Fixed Nitrogen Laboratory (2). Figure 2 is a flow sheet of the apparatus.

PROCEDURE. The bombs were immersed in a molten salt bath (50 per cent potassium nitrate and 50 per cent sodium nitrate) and brought to the desired temperature before a charge of cracking stock was forced into the reaction bomb:

At the start of a run (Figure 1) bomb 1 was filled with molten solder, and a small amount of solder was also present

An experimental cracking apparatus has been constructed, on a laboratory scale, which gives the following data, within the degree of accuracy required for the design and operation of commercial cracking plants: (1) yields of gas, gasoline, coke, and polymers as a function of measured time, temperature, and pressure; (2) specific volume data as a function of measured time, temperature, and pressure.

The rates of reaction for the several cracked products have been computed and are found to agree well with the results of other laboratory investigators. The specific volume data have been used in comparing the reaction rates found in this laboratory with actual plant operations. As a result of this laboratory investigation, a new basis has been found for the design of cracking plants.

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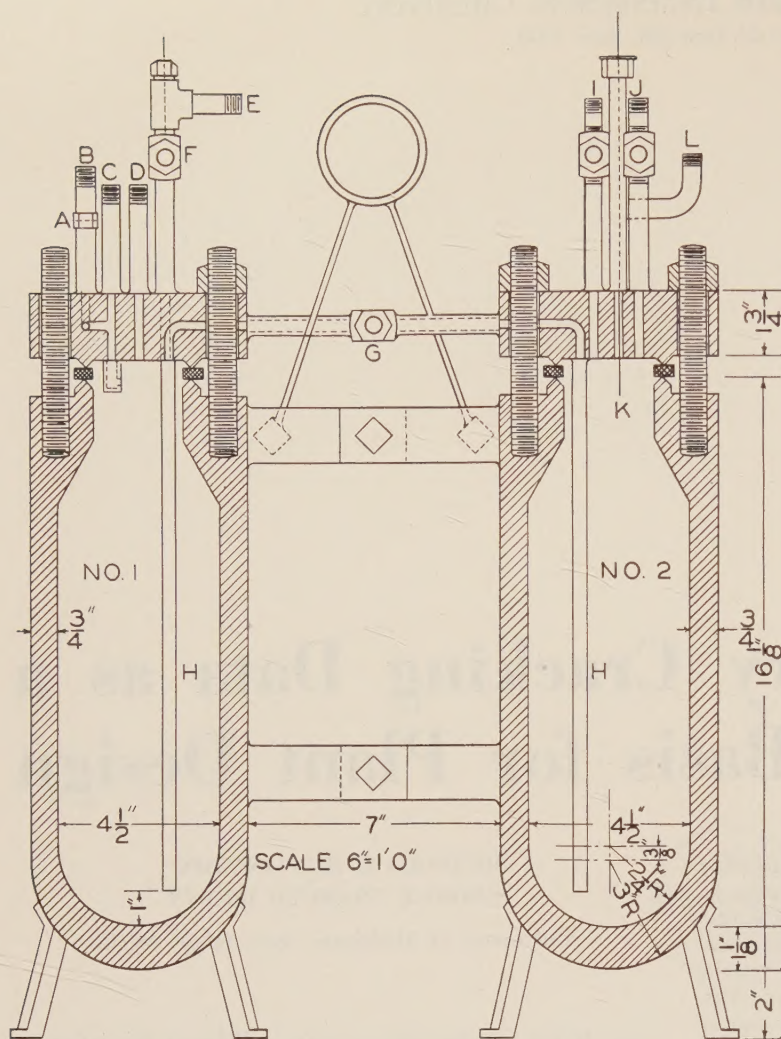


FIGURE 1. CRACKING BOMBS

- | | |
|---------------------------|---------------------------|
| 1. Reaction bomb | F. Vapor delivery valve |
| 2. Nitrogen bomb | G. Pressure control valve |
| 3. Rupture disk | H. Solder transfer line |
| 4. Relief line | I. Nitrogen delivery line |
| 5. Pressure and feed line | J. Nitrogen pressure line |
| 6. Thermocouple well | K. Warning wire |
| 7. Vapor delivery line | L. Pressure connection |

in the bottom of bomb 2, which was filled with nitrogen at atmospheric pressure. The oil was charged into bomb 1 through *C*, causing the pressure to build up quickly to the level desired, after which the pressure was maintained constant by the release of molten solder through a manually throttled valve, *G*, located in the transfer line between the two bombs. Temperature readings were taken at frequent intervals, especially during the heating period, by means of an iron-constantan thermocouple which projected into the reaction zone through connection *D*. Pressures were recorded by means of a carefully calibrated Bourdon gage connected to *B*. The increase in volume in the cracking zone was obtained from time to time by the measurement of the nitrogen displaced from bomb 2 through connection *J*. After the run had proceeded for the desired length of time, valve *G* was closed and the products were discharged from the reaction zone by opening valve *F*. As soon as the pressure on bomb 1 had fallen to 10 pounds per square inch gage, valve *G* was opened and the solder from bomb 2 was forced into bomb 1 so as to complete the removal of all the products from the reaction zone. The products were cooled to about 60° F.; and the uncondensed vapors were metered and passed through activated gasoline charcoal in order to recover the natural gasoline fractions. The levels of molten solder were then equalized and the bombs were removed from the bath and allowed to cool, in preparation for the removal of coke from bomb 1.

MATERIAL USED. A combined feed from a commercial cracking plant, containing about 75 per cent of recycled material, was used in all of the experimental runs. Its physical properties were:

(A. P. I. gravity = 24.8° at 60° F.)

Engler Distillation, ° F.	True Boiling Point Distillation, ° F.
Initial b. p.	Initial b. p.
10% by vol.	6.43% by vol.
30% by vol.	28.70% by vol.
50% by vol.	55.25% by vol.
70% by vol.	75.30% by vol.
	91.40% by vol.
	180
	390
	450
	525
	600
	700

RESULTS. The results of the experimental work are summarized in Table I, except some density measurements given in Table II which were used in correlating actual plant data.

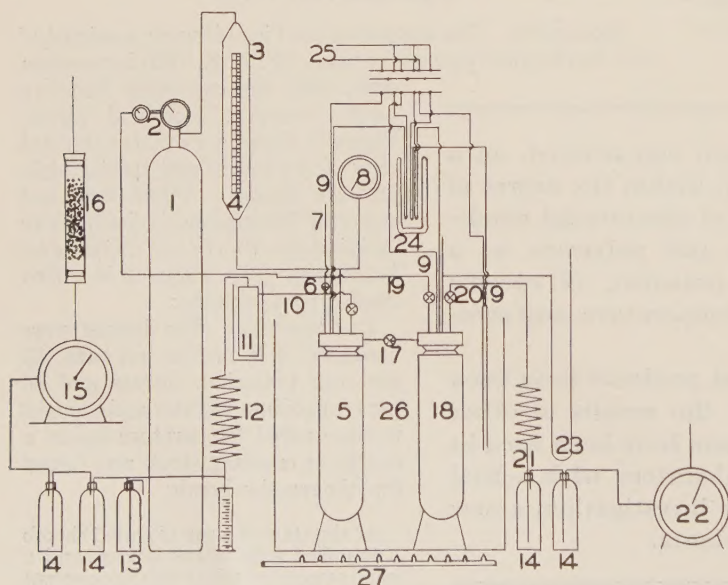


FIGURE 2. FLOW SHEET OF EXPERIMENTAL APPARATUS

- | | |
|--------------------------|----------------------------|
| 1. Nitrogen cylinder | 15. Vapor meter |
| 2. Reducing gage | 16. Charcoal absorber |
| 3. Charging cylinder | 17. Pressure control valve |
| 4. Gage glass | 18. Nitrogen bomb |
| 5. Reaction bomb | 19. Nitrogen pressure |
| 6. Rupture disk | 20. Nitrogen delivery |
| 7. Relief line | 21. Cooler |
| 8. Bourdon pressure gage | 22. Wet test meter |
| 9. Thermocouples | 23. Mercury manometer |
| 10. Vapor delivery line | 24. Thermos bottle |
| 11. Scrubber | 25. To potentiometer |
| 12. Iced condenser | 26. Salt bath |
| 13. Sampling bottle | 27. Gas burners |
| 14. Water saturators | |

TABLE I. EXPERIMENTAL RESULTS

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Run	Pressure, Lb./Sq. In. Gage	Temp., ° F.	Effective Time, Min.	Vol. % 390° F. End Point + Loss Column Dist.	Vol. % Engler 2(284 + Loss)	Vol. % Charcoal Gasoline	6-7, Total 390° F. End Point Gasoline by Vol.	Vol. % 330° F. Cut + Loss Column Dist.	Vol. % 340° F. Cut + Engler Dist.	7-10, Total Vol. % 340° F. End Point Gasoline	% by Weight Dry Gas	% by Weight Coke	% Heavy Material Left in Bomb	13-14, Total Polymers and Coke
46	900	794	102.59	13.30	11.06	1.05	12.11	9.68	8.75	9.80	2.47	0.35	2.65	3.00
47	...	...	117.21	...	...	...	...	...	...	...	...	0.365	...	...
48	...	...	167.80	13.70	12.00	1.35	13.35	11.50	10.70	12.05	3.80	0.46	0.89	1.35
45	...	...	205.80	12.35	14.45	1.90	18.35	11.10	13.00	4.55	4.55	0.64	6.99	7.63
36	...	...	392.50	18.00	20.40	3.35	23.75	13.50	14.10	17.45	7.74	1.56	7.09	8.65
25	600	794	178.50	12.90	...	1.74	14.64	11.60	...	13.34	3.70	0.74	7.47	8.21
26	...	...	68.17	10.06	...	0.26	10.32	7.45	0.26	7.71	0.55	0.22	5.26	5.48
27	...	...	241.65	15.90	...	2.00	17.90	11.45	2.00	13.45	4.53	1.11	9.86	10.97
24	300	794	55.20	10.75	9.83	0.45	7.60	8.05	5.81	6.26	1.07	0.28	8.03	8.31
29	...	...	82.73	9.60	7.92	0.72	8.71	8.20	7.31	8.10	1.91	1.58	6.65	8.23
30	...	...	82.63	...	10.20	0.79	10.92	...	8.25	8.97	1.64	1.61	0.52	2.13
9	...	...	137.40	...	8.48	0.94	9.42	...	7.22	8.16	2.20	0.83	7.31	8.14
7	300	779	74.41	...	4.58	0.43	5.01	...	3.50	3.93	1.04	0.87	3.99	4.86
33	300	744	180.22	6.24	4.81	0.28	5.09	...	...	...	0.73	0.32	2.64	2.96
31	...	...	338.19	8.60	6.60	0.54	7.14	...	...	...	1.28	0.23	3.81	4.04
32	...	...	421.95	7.86	7.29	0.65	7.94	...	...	...	1.60	0.56	5.48	6.04
51	900	844	40.50	18.50	18.38	2.14	20.52	14.45	14.35	16.49	5.42	0.48	3.05	3.53
52	...	...	58.32	...	...	...	...	...	...	...	...	1.16	...	...
53	...	...	61.03	20.82	19.83	2.89	22.72	15.56	15.95	18.84	7.56	1.02	1.22	2.24
49	...	...	89.00	16.10	19.00	3.70	22.70	...	14.30	18.00	9.69	3.29	9.41	12.70
50	...	...	92.06	16.90	16.45	3.67	20.12	13.30	12.75	16.42	9.51	3.12	5.88	9.00
62	...	...	253.56	...	14.90	5.83	20.73	...	10.60	16.43	13.64	10.80	12.84	23.64
20	600	844	27.95	...	...	...	...	...	...	...	...	...	...	...
21	...	...	88.47	19.80	...	1.67	21.47	16.10	...	17.77	4.17	1.96	7.38	9.34
23	...	...	35.77	13.60	...	1.49	14.99	11.20	...	12.69	3.69	0.80	9.16	9.96
18	...	...	41.27	...	16.24	1.78	18.02	...	12.40	14.18	5.45	0.92	4.86	5.73
19	...	...	40.00	...	16.24	1.78	18.02	...	12.90	14.68	4.91	0.93	1.90	2.83
42	...	...	138.91	15.90	16.92	4.72	21.64	11.78	12.35	17.07	10.64	8.00	11.03	12.03
43	...	...	167.72	16.75	17.90	5.41	23.31	12.40	13.03	18.44	12.39	8.18	4.91	13.09
22	...	...	186.20	14.90	...	5.04	19.94	12.40	...	17.44	13.34	7.82	6.08	13.90
17	500	844	25.38	...	11.70	1.46	13.16	12.60	...	14.06	3.79	0.41	4.77	5.18
15	...	...	27.33	13.00	12.97	1.60	14.57	13.00	...	14.60	4.14	0.46	4.47	4.93
12	300	844	16.37	10.63	...	0.81	11.44	...	7.65	8.46	1.78	1.04	5.61	6.65
13	...	...	17.80	...	9.02	0.89	9.91	...	7.43	8.32	2.25	1.03	5.09	6.12
16	...	...	15.06	10.92	7.29	0.57	7.86	5.37	6.84	7.41	1.39	0.38	2.83	3.21
14	...	...	39.49	...	13.27	1.91	15.18	...	9.30	11.21	4.98	1.51	3.70	5.21
57	600	894	13.07	...	19.70	2.43	22.13	...	13.75	16.18	6.35	1.56	7.07	8.63
58	...	...	9.60	21.00	19.85	1.89	21.73	18.70	15.70	17.58	4.83	1.07	1.57	2.64
54	...	...	15.50	...	18.50	3.60	22.10	13.90	14.40	18.00	8.89	2.98	5.99	8.97
55	...	...	15.14	19.00	20.92	3.34	24.26	...	16.30	19.64	8.29	2.62	0.08	2.70
59	...	...	13.10	...	21.65	2.35	24.00	...	15.50	17.85	5.53	1.55	4.76	6.31
60	...	...	30.84	...	20.55	4.90	25.45	...	15.85	20.75	12.14	4.70	3.69	8.39
61	...	...	18.82	...	22.84	3.17	26.01	...	14.25	17.42	8.16	3.48	3.12	6.60
38	...	...	42.20	...	...	5.52	...	...	11.20	16.72	12.38	6.20	13.72	19.92
39	...	...	41.72	...	16.85	6.30	23.15	...	12.00	18.30	13.59	6.22	7.23	13.45
34	...	...	10.00	...	...	...	...	...	...	...	...	...	...	...
35	...	...	51.00	...	15.15	6.67	21.82	...	11.50	17.17	15.08	7.05	9.05	16.10
36	...	...	87.10	...	12.47	5.54	18.01	...	...	...	13.03	7.40	17.65	25.05
37	...	...	86.97	...	10.80	7.50	18.30	...	...	...	17.19	7.22	12.08	19.30
40	300	894	49.50	...	11.10	5.54	16.64	...	8.70	14.24	12.42	6.10	16.16	22.26
41	...	...	50.50	...	11.80	6.17	17.97	...	9.44	16.14	13.70	6.10	9.13	15.23

The effective time at the cracking temperature was calculated for each run from the actual time and temperature-time curve by assuming, as a first approximation, that the cracking rate doubles for each rise in temperature of 18° F. Upon plotting the yields as a function of effective time, it was found that the cracking rate for the formation of (coke, gas, and gasoline) doubled for a rise in temperature from 19° to 22° F. Using these values as a second approximation changed the effective time less than one-half minute for those runs where the actual time varied most from the effective time. Since this small variation in time was well within the range of experimental error, a second series of calculations on effective time was not made.

Discussion

A definition of gasoline is necessary before calculations of the gasoline yields from the various experimental runs can be made. Since the refinery, from which the combined feed was taken for this experimental work, was producing a 64.2° A. P. I., 339° F. end point, stabilized gasoline at that time, it was decided that one set of calculations should be made with this product as a basis. Good and Connell (8) show the

correlation between A.S.T.M. and laboratory column distillations, on which a 330° F. cut temperature on a column gives a distillate of 340° F. end point in the A.S.T.M. distillation. This relationship was found to apply satisfactorily to distillations of the cracked products made in this investigation. As the refinery was recovering stabilized natural gasoline, the charcoal recovery gasoline yield produced in this laboratory was added to the amount recovered by the distillation of the recovered liquid. The vapor loss from the distillations was also taken as part of the gasoline yield, because of the imperfect condensation of lighter gasoline fractions in the laboratory apparatus.

Because it was impossible to obtain sufficient material from the cracking experiments at the lower pressures and long times for an adequate column distillation, it is necessary that some other means of determining the gasoline content of the recovered liquid be found.

The initial boiling point on the 100-cc. Engler distillation of the charging stock is 342° F. If the cut at 340° F. on this distillation is taken as representative of the gasoline at 340° F. end point, the results will be consistent in that the charging material will be free of such gasoline. Furthermore, this

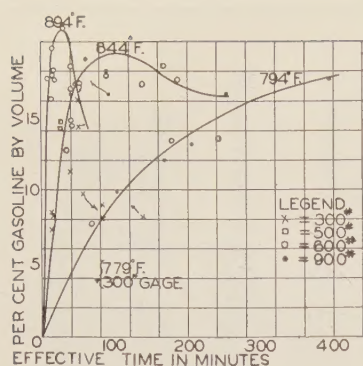


FIGURE 3. PER CENT GASOLINE (PER CENT BY VOLUME CHARCOAL RECOVERY + 340° F. CUT ON ENGLER) FORMED AS A FUNCTION OF TIME

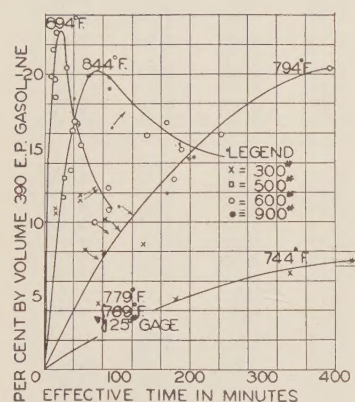


FIGURE 4. PER CENT GASOLINE (390° F. END POINT) vs. TIME

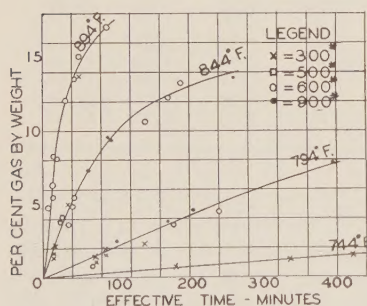


FIGURE 5. PER CENT DRY GAS FORMED AS A FUNCTION OF TIME

pressure within this range does not appear to be noticeable.

Gasoline Formation

In order to compare these results with those of other investigators, it is necessary that gasoline be defined in approximately the same manner.

Geniesse and Reuter (6) determined gasoline yields by means of column distillations, which were correlated in some unexplained manner with A. S. T. M. distillations, and as a result set up a hypothetical gasoline having a 10 per cent point of 140° F., 54 per cent of 284° F., and 90 per cent point not higher than 392° F. Keith, Ward, and Rubin (13) actually produced gasoline of 400° F. end point with an average 50 per cent point of 260° to 290° F. The gasoline vapors,

method of determining the gasoline content of a petroleum fraction has been widely used in the petroleum industry for many years and was found satisfactory for estimating the content of the more volatile gasoline such as that under consideration. Comparison of the gasoline content determined as this 340° F. cut with that determined by the column distillation cut at 330° F. indicates good agreement between the two methods. For this reason and because 100-cc. Engler distillations were made on the liquid samples recovered from all runs, the 340° F. end-point liquid gasoline made during the cracking operation is defined as the percentage cut at 340° F. in the Engler distillation.

Figure 3 gives the percentage by volume of the 340° end-point gasoline as determined by the Engler distillation, plus the charcoal recovery gasoline, as a function of effective time for constant temperature. All runs were made at constant pressures which ranged from 300 to 900 pounds per square inch gage. The effect of pressure within this range does not appear to be noticeable.

including the butanes, were condensed and included in their 400° end-point product, but apparently this was not done by Geniesse and Reuter.

A cut at 390° F. in a column distillation gives a distillate having a 390° F. end point in the A. S. T. M. distillation (8). Since most of the liquid samples recovered from the cracking runs in this investigation were not large enough for both A. S. T. M. and column distillations, A. S. T. M. tests were made in all cases and column distillations when possible. It was thought that the percentage at 284° F. on the A. S. T. M. when doubled might equal the percentage of gasoline cut at 390° F. on the column.

The amount of gasoline in the combined feed could not be taken as the percentage up to 390° F. on the column distillation, as only 0.7 per cent came over up to 284° F. and 6.1 per cent from 284° to 390° F., showing that the greater portion of this 390° F. cut was actually a naphtha fraction. Since the gasoline was to have a maximum temperature of 284° F. at its 50 per cent point, the percentage over at 390° F. on the column could be taken as gasoline only on those tests showing a 50 per cent point, of the 390° F. cut, at 284° F. or less. Whenever the 50 per cent of the 390° F. cut in the column distillation showed a higher temperature than 284°, twice the percentage at 284° F. was found to correspond to the yield of gasoline with 50 per cent distilled at 284° F. or less. Therefore the amount of gasoline in the original material was taken as 2×0.7 or 1.4 per cent.

Because the loss in distillation of the recovered liquid is a laboratory loss due to incomplete condensation of light fractions of gasoline, this loss was added to the amount of condensate recovered by either the column or the A. S. T. M. distilla-

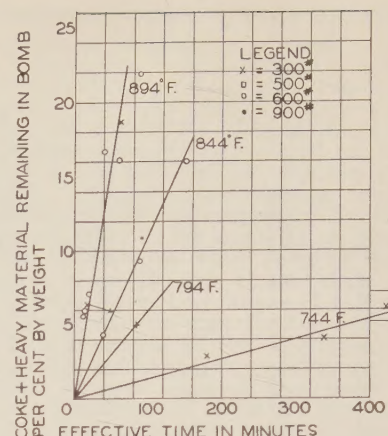


FIGURE 6. PER CENT POLYMERS FORMED AS A FUNCTION OF TIME

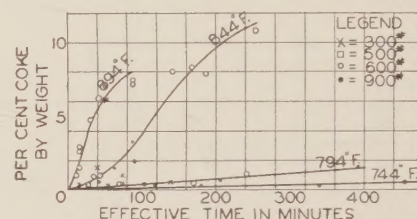


FIGURE 7. PER CENT COKE FORMED AS A FUNCTION OF TIME

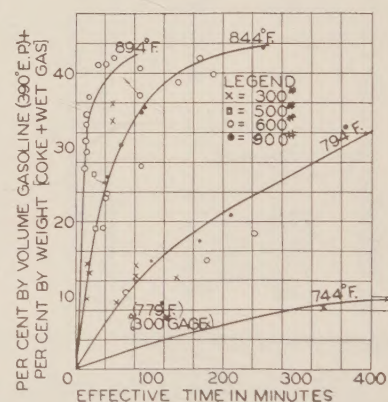


FIGURE 8. COKE + WET GAS + GASOLINE (390° F. END POINT) FORMED AS A FUNCTION OF TIME

tion. In the latter distillation 0.5 per cent was retained as residue by the distilling flask; hence this amount was deducted from the gross loss to give the actual gasoline vapor loss.

Column 5, Table I, shows the percentage of gasoline as determined by column distillations in the manner described, and column 6 shows the percentage as determined by taking twice the percentage over at 284° F. on the A. S. T. M. distillation. In all except a few cases, where erroneous material balances were obtained on column distillations, the agreement is within the range of experimental error. Therefore twice the percentage over at 284° F. on the A. S. T. M. was used as the percentage of 390° F. end-point gasoline in the "cracked" liquid, recovered from each experimental run.

Figure 4 shows the percentage by volume of 390° end-point gasoline, so defined, in the recovered liquid as a function of effective time, for constant temperature. Maxima are reached for the 844° and 894° F. lines, and such peaks would probably have been reached for 744° and 794° F. temperatures with longer periods of cracking. Geniesse and Reuter (6) showed maxima for gasoline yields, with increasingly higher peaks for decreasing temperatures, but a different oil was used and the oil was in the vapor phase at atmospheric pressure during the entire cracking operation.

Gas Yields

The yield of dry gas has been calculated as the percentage by weight of the original charge, and these percentages are shown in Figure 5 *vs.* effective time with lines of constant temperature. Within the limits of accuracy of these tests, variation of pressure between 300 and 900 pounds per square inch gage seems to have little or no effect. Keith, Ward, and Rubin (13) have found that lower pressures favor gas production, but above 500 pounds the effect is negligible.

Polymerization and Coke Formation

"Polymers" may be defined as those products of higher molecular weight such as asphalt, tar, etc., which are always formed in a cracking operation, and coke into which they may be converted. It was found that the apparent loss of material whenever a balance was made after each "cracking" run, was due to the retention of heavy polymers and coke in the clearance space of the nipples in the top of the bomb cap. This fact was verified by reason of the consistently higher loss of 10 to 15 cc. following the first run after the bomb

was cleaned out, compared with a check run made immediately afterwards, without the removal of the bomb cap. Whenever the bomb caps were removed, the heavy polymers disappeared as smoke or were converted into coke which adhered to the inside walls of the reaction bomb. Material left in the bomb at the end of each run was evidently higher in boiling point than the temperature at which the particular run was made, since the pressure on the bomb was reduced to atmospheric as the products were released. In determining the yield of heavy polymers and coke, the coke plus the average amount of material remaining in the bomb after a run and the following check run was considered to be a fair measure of polymerization. The data for such double runs are plotted on Figure 6, and, although the points are somewhat scattered, the trend for each temperature is clearly defined.

Figure 7 shows that the coke formation is slower in getting under way than the gas or gasoline, which is in accordance with the theory that coke is not a primary product of cracking but is formed as a result of secondary reactions such as polymerization.

Figure 8 gives the percentage of (wet gas plus 390° end-point gasoline plus coke) *vs.* effective time with lines of constant temperature.

Velocity of Reactions

Since gasoline is the most valuable product of a cracking operation, a study of the rate of its formation is of primary importance. The refiner has always calculated gasoline yields by volume per cent, and the public thinks of gasoline in terms of gallons instead of pounds. Previous investigators (6, 13) have reported gasoline yields in volume percentages. For these reasons only has gasoline been calculated on a volume basis in this paper. From the standpoint of simplicity, the weight basis should be used for all yields such as gas, gasoline, "polymers," and coke. From a scientific viewpoint, mole percentages would give a better insight into the rate of chemical reaction.

Previous investigators have found that the monomolecular reaction rate holds true for incipient cracking, but that this rate falls off as parallel and consecutive reactions set in and change the nature of the original material.

The over-all monomolecular rates of formation of gas, gasoline, and coke have been determined by extrapolation to zero percentage cracked (Figure 9); and these rates have

TABLE II. ORIGINAL DATA ON DENSITIES OF THE COMBINED FEED DURING SEVERAL CRACKING RUNS

	Crack- ing Temp., ° F.	Min. Effec- tive Time	—N ₂ Meter—		Increase in Vol., Cu. Ft.		Cu. ft. per lb.	Caled. Sp. Vol. Add 0.005 cu. ft. for clear- ance, cu. ft./lb.
			Cu. ft. as recorded	Temp. meter, ° F.	Δ	Σ		
Run 31 at 300 lb. gage, 744° F.; charge = 1.09 lb.	...	0.0	0.2942	80	0.0095	0.0095	0.0181	0.0239
	684	0.07	0.3037		0.0009	0.0104	0.0197	0.0247
	730	2.79	0.3046		0.0003	0.0107	0.0203	0.0253
	740	12.04	0.3049					
Run 20 at 600 lb. gage, 844° F.; charge = 0.512 lb.	...	0.0	0.7235	85	0.0058	0.0058	0.0257	0.0307
	837	4.28	0.7293		0.0007	0.0065	0.0288	0.0338
	841	7.22	0.7300					
Run 49 at 900 lb. gage, 844° F.; charge = 1.075 lb.	...	0.0	0.5653	87	0.0095	0.0095	0.0230	0.0280
	833	2.42	0.5748		0.0012	0.0107	0.0259	0.0309
	843	10.77	0.5760					
Run 40 at 300 lb. gage, 894° F.; charge = 0.1935 lb.	...	0.0	0.8951	93	0.0059	0.0059	0.071	0.076
	872	0.80	0.9010		0.0055	0.0114	0.138	0.143
	879	2.02	0.9065		0.0023	0.0137	0.166	0.171
	885	3.49	0.9088		0.0048	0.0185	0.224	0.229
	891	7.60	0.9136		0.0035	0.0220	0.266	0.271
	893	12.34	0.9171		0.0022	0.0242	0.293	0.298
	893	17.07	0.9193					
Run 38 at 600 lb. gage, 894° F.; charge = 0.43 lb.	...	0.0	0.5484	98	0.0044	0.0044	0.0239	0.0289
	877	1.21	0.5528		0.0044	0.0088	0.0478	0.0528
	899	2.91	0.5572		0.0090	0.0178	0.0966	0.1016
	898	8.01	0.5662		0.0076	0.0254	0.1370	0.1420
	903	15.81	0.5738					

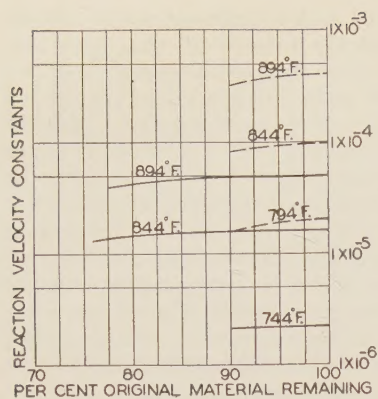


FIGURE 9. REACTION VELOCITY CONSTANTS FOR FORMATION OF GAS, GASOLINE, AND COKE AS A FUNCTION OF ORIGINAL MATERIAL REMAINING

--- 100 per cent less (390° F. end-point gasoline + wet gas + coke)
 - - - 100 per cent less (390° F. end-point gasoline)

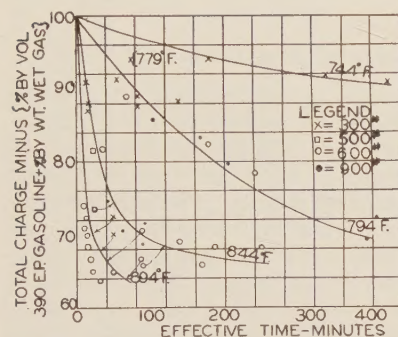


FIGURE 12. TOTAL CHARGE, LESS WET GAS AND 390° F. END-POINT GASOLINE, AS A FUNCTION OF TIME

$$K = \frac{1}{t} \ln \frac{A'}{A' - x}$$

where K = reaction velocity constant, sec.

t = time, sec.

A' = 100, or per cent of original material

x = per cent conversion at any time, t

(Gasoline = volume per cent; gas = weight per cent; coke = weight per cent)

The curves obtained by Geniesse and Reuter (6) and by Keith, Ward, and Rubin (13) show somewhat higher reaction rates which are probably due to the fact that virgin gas oils were used in these previous investigations, whereas the combined feed used in this present work consists of a mixture of three parts of reflux which has been cracked in a recycling operation, and one part of virgin gas oil.

The energy of activation can be calculated by means of the Arrhenius equation which, in its integrated form, is

$$\ln K = \frac{-E}{RT} - C$$

where K = reaction velocity constant

E = energy of activation, cal.

R = gas constant, 1.985

T = abs. temp., °K.

C = integration constant

Two values of K are required for the solution of E and C which are the only unknowns. For the formation of (gas, 390° F. end-point gasoline, and coke), the energy of activation is 59,200 calories and $C = 32.55$. For the formation of 390° F. end-point gasoline, $E = 56,100$ calories and $C = 30.15$. Geniesse and Reuter (6) found a value of 53,400

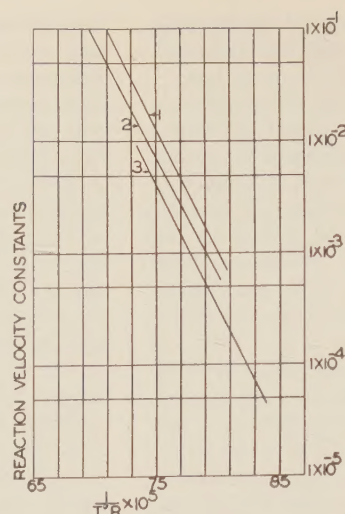


FIGURE 10. INITIAL REACTION VELOCITY CONSTANTS AS A FUNCTION OF THE RECIPROCAL OF ABSOLUTE TEMPERATURE

1. 390° F. end-point gasoline + wet gas (Keith, Ward, and Rubin)
2. 390° F. end-point gasoline + wet gas + coke (Geniesse and Reuter)
3. 390° F. end-point gasoline + wet gas + coke (Huntington and Brown)

been plotted in Figure 10 vs. the reciprocal of the absolute temperature. The monomolecular reaction equation used in these calculations is:

calories for (gas, gasoline, and coke) formation while Keith, Ward, and Rubin (13) obtained 57,100 calories for the formation of (gas and gasoline).

Although the over-all rates of (gas, gasoline, and coke) formation do follow the monomolecular reaction rate initially, a more critical study of each one of

these products shows the cracking process to be far from simple. The several reactions which probably take place may be simplified and represented by the diagrammatic Figure 11. An alphabetical nomenclature has been given to the original material and the several products in order to simplify the formation of certain over-all reaction rates.

Reactions 1, 2, 3, and 7 probably take place in one direction only; 4 is slightly reversible, and 5 and 6 are largely reversible.

From Figures 3 and 4 the rate of production of gasoline indicates that it is controlled by two simultaneous reactions, one involving formation, and the other disappearance into gas. The rate of formation is dependent upon the percentage of original material left at any time, t (Figure 12), and the rate of disappearance is based upon the percentage of gasoline present and its tendencies to crack into gas. These two simultaneous first-order reactions might be formulated as follows:

$$\frac{dL}{dt} = K_2A - K_4(L)$$

where K_4 = rate of cracking gasoline

K_2 might be the initial cracking rate obtained by extrapolating the monomolecular reaction rate to zero per cent transformed. K_4 can be obtained since $dL/dt = 0$ when the maximum gasoline yield is obtained. At that time,

$$\frac{K_2A}{K_4} = \frac{L}{A}$$

or

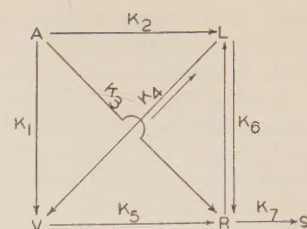


FIGURE 11. DIAGRAM OF CRACKING AND POLYMERIZATION REACTIONS

- A. Original feed
- L. Cracked gasoline
- V. Cracked gas
- R. Liquid residue
- S. Solid coke
- G. $L + V$

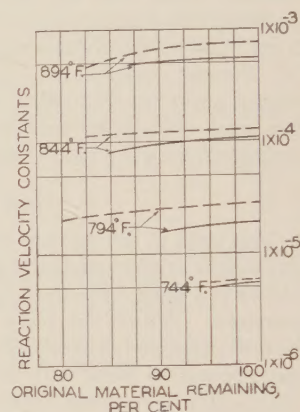


FIGURE 13. REACTION VELOCITY CONSTANTS FOR POLYMERIZATION AS A FUNCTION OF THE ORIGINAL MATERIAL REMAINING

Same designation as in Figure 9.

For 894° F. (Figure 4), $t = 1380$ seconds and $L = 23$ per cent by volume, at the peak:

$$A = 100 - (\text{wet gas, } 390^\circ \text{ end-point gasoline and total polymers}) = 62.3\% \text{ (Figures 12 and 6)}$$

$$K_2 = 0.000545 \text{ (Figure 9)}$$

$$\text{Solving, } K_4 = K_2 \left(\frac{A}{L} \right) = 0.000545 \times \frac{62.3}{23.0} = 0.001475 \text{ or } \frac{K_4}{K_2} = 2.71 \text{ for } 894^\circ \text{ F.}$$

For 844° F., $t = 4320$ and $L = 20.25$:

$$A = 62.7; K_2 = 0.00011$$

$$K_4 = 0.00011 \times \frac{62.7}{20.25} = 0.000344 \text{ or } \frac{K_4}{K_2} = 3.10 \text{ for } 844^\circ \text{ F.}$$

In arriving at the comparative rates of formation and decomposition, it was assumed that all of the original material which did not go to form gas, gasoline, and heavy polymers remained unchanged. This is not the case, since the original material is, no doubt, being transformed into other products boiling in the naphtha-kerosene range which are more resistant toward cracking. Taking the coefficients obtained by Schultz and White (19) as a measure of the rate of cracking gasoline, it is seen that the combined feed cracks about twelve times as fast as gasoline initially, or

$$\frac{K_2}{K_4} = \frac{12}{1} = \frac{L}{A}$$

Since L equals 23 per cent at the maximum for 890° F., A would be only about 2 per cent. In other words, practically all of the original material would have been transformed into more highly "thermolized" products by the time the peak of gasoline production has been reached. That the original charging stock should become more resistant towards cracking is in agreement with the results of other investigators (6, 14, 18) who have found that the amount of "crack" per pass falls off with time.

Rate of Polymerization

As indicated from the data of Figure 7, the formation of coke is a secondary reaction and is probably the result of a form of polymerization.

From the diagram of the reactions (Figure 11), the rate of polymerization is proportional to the activity of the polymerizable material which is left after the removal of gas and gasoline. Since the first polymers which are formed are probably lower in molecular weight than the heavy polymers which go to make up R and S , let Z equal the percentage of intermediate-boiling polymers, heavier than gasoline and lighter than the heavy viscous residuum. As the combined feed consists of a mixture containing 75 per cent of recycle material, Z will be approximately equal to $(A' - G)$ after a short period of cracking. As was brought out in the discussion of the formation and decomposition of gasoline, it appears likely that the percentage of original material falls to a low figure by the time the maximum gasoline yield is reached. The rate of polymerization may therefore be formulated:

$$\frac{dP}{dt} = K_2(a_Z)^N - K_{GP}(P)$$

where a = activity or effective concn. of Z

By making the following assumptions, the foregoing equation may be simplified:

- (1) $K_{GP}(P)$, the rate of decomposition of P into gas and gasoline may be disregarded.
- (2) Let N equal 2.

(3) The activity of Z is proportional to Z/A' . If a liquid is present, the activity of Z will be proportional to its mole fraction in the liquid. The separation of gas and gasoline vapors may be considered to compensate for the decrease in molecular weight; i. e., as cracking proceeds and the molecular weight decreases, separation of vapors are just sufficient to maintain the same number of moles in the liquid. Then:

$$(4) Z = (A' - G).$$

Taking these simplifying assumptions into consideration:

$$\frac{dP}{dt} = K_p(A' - G)^2.$$

$$\text{or } \int_0^P \frac{dP}{(A' - G)^2} = K_p \int_0^t dt$$

where K_p = sp. rate of polymerization

This expression has been integrated graphically and the results are shown in Figure 13. The fact that the rate falls off with time is an indication that the activity of the polymerizable material is being reduced by the dilution of the liquid phase with less active gasoline fractions. If such is the case, increasing pressures within the range of the presence of two phases should reduce the tendency for polymers of intermediate molecular weight in the liquid to form heavy polymers and coke.

The increase in temperature required to double the rate of polymerization averages about 33° between 744° and 894° F. while that for doubling the rate of gasoline formation is between 20° and 22° F. for the same temperature range. This fact indicates that high temperatures and short times are more favorable than low temperatures and long times from the standpoint of gasoline production within the range of temperatures studied.

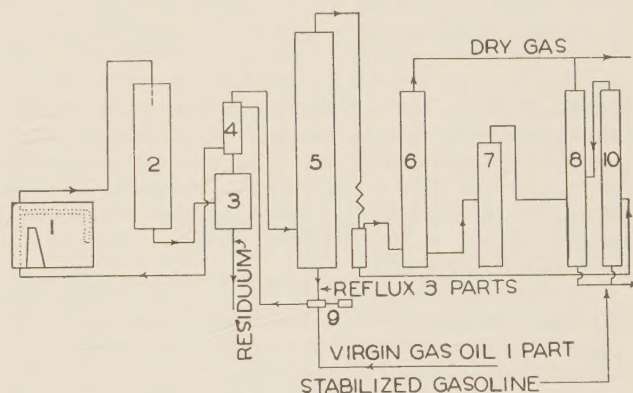


FIGURE 14. FLOW SHEET OF COMBINED CRACKING AND GASOLINE RECOVERY UNIT

- | | |
|-----------------------|-----------------|
| 1. Pipe still furnace | 6. Absorber |
| 2. Reaction chamber | 7. Still |
| 3. Flash chamber | 8. Stabilizer |
| 4. Heat exchanger | 9. Charge pump |
| 5. Fractionator | 10. Debutanizer |

Correlation of Laboratory Results with Plant Data

The data reported above on the rates of gas, gasoline, polymer and coke formation were obtained on the combined feed used in a commercial cracking plant. The application of these laboratory data to the analysis of the operation of this cracking plant will make clear how such laboratory data may be used for the satisfactory design of cracking plants.

The cracking plant under consideration had a flow sheet which was essentially the same as shown in Figure 14.

TABLE III. CALCULATED PRESSURE

Pipe Section	Length	Equivalent Length, N	D	U_2	U_1	U_{av}	1	2	Av.	T_2	T_1	Z_2	Z_1
0-48	1440	2190	3.75	12.85	11.60	12.23	44.90	40.80	42.85	715	570	0.15	0.23
48-87	1170	1780	3.75	15.20	12.85	14.02	40.80	34.50	37.65	845	715	0.12	0.16
87-113	780	1065	3.75	18.30	15.20	16.75	34.50	28.60	31.55	905	845	0.11	0.12
113-135	660	1005	4.00	20.90	18.30	19.60	28.60	25.00	26.80	940	905	0.115	0.11
135-150	450	684	3.95	25.20	20.90	23.05	25.00	20.80	22.90	940	940	0.125	0.115
135-150	450	684	3.95	30.80	20.90	25.85	25.00	11.10	17.00	940	940	0.135	0.115
150-158	240	365	3.90	59.20	30.80	45.00	11.10	6.67	8.87	940	940	0.145	0.135

^a Two approximations were made on tube section 135-150. Equivalent length of return bends was equal to 50 diameters. Viscosity of liquid increased as vaporization and cracking took place. Decreasing diameter of 4-inch pipe after tube 113 was due to coke formation. Friction factor increased from that of a smooth pipe at entrance to that of a very rough pipe near the exit, because of the uneven deposition of coke. In computing elapsed time at any temperature the rate of cracking was assumed to double for a rise in temperature of 22° F.

Refinery Operating Data

The following plant data were obtained from the run during which the laboratory samples were taken:

Charge = 2750 bbl. virgin gas oil per 24 hr.
 Length of run = 274 hr. at reflux ratio of 3:1
 Rate of charging the virgin gas oil =

$$\frac{2750 \times 42 \times 8.34 \times 0.8364}{86,400} = 9.42 \text{ lb. per sec.}$$

Pressure, lb./sq. in. gage:
 Charge pump = 970
 Entering furnace = 830
 Reaction chamber = 400
 Flash chamber = 85
 Temperature, ° F.:
 To furnace = 570
 To radiant section = 720
 Tube 113 = 910
 Entering flash chamber = 785
 Leaving flash chamber = 710

The actual temperature in the reaction chamber was not given, but during a previous run when the temperature of the oil from the furnace was 900° F. the temperatures in the reaction chamber were as follows: top, 835° F.; center, 850° F.; bottom, 855° F. This indicates a 45° drop. The low temperature in the top was no doubt due to the stagnant condition of the vapors in that part of the chamber, because the feed nipple stuck down several feet into the vessel. The temperature for the vapors in the reaction chamber in this run was taken as 895° F., which corresponds to the 45° drop in temperature in the former run.

The reaction chamber was 10 feet o. d. and 40 feet high. The flash chamber was 10 feet o. d. and 15 feet high. The walls of the reaction chamber were about 3 inches thick and of the flash chamber, about 1.0 inch thick.

At the end of the run 6 inches of coke were found on the inside walls of the reaction chamber. This coke weighed 10 tons. The total weight of the combined feed to the furnace was $(4 \times 2750 \times 42 \times 274 \times 834 \times 0.9)/(1 \times 2000 \times 24) = 19,800$ tons for the entire run.

The percentage by weight of coke formed in the reaction chamber was $(10 \times 100)/19,800 = 0.50$ (based on the combined feed).

The percentage by weight of coke in the flash chamber = $(0.5 \times 100)/19,800 = 0.0025$ (based on the combined feed).

The percentage by volume of residual oil withdrawn continuously from the flash chamber was 11.60, based on the virgin gas oil. Its A. P. I. gravity was 7.6°.

The percentage of stabilized gasoline was 75.7 per cent, based on the virgin oil.

The stabilized gasoline had an A. P. I. gravity of 64.10° and an A. S. T. M. distillation as follows:

Initial b. p. = 82° F.	90% = 316° F.
10% = 120° F.	End point = 339° F.
50% = 221° F.	Recovery = 96 per cent

ANALYSIS OF PIPE STILL FURNACE OPERATION. Before a determination could be made of the cracking time in the reaction chamber, an analysis of the furnace operation was required so that the density of the charge leaving the furnace might be known. This called for an analysis of the pressure drops through several sections of the pipe still. According to the flow formula for fluids, given by McAdams (16) for turbulent flow in straight pipes:

$$P_1 - P_2 = \frac{G^2 (V_2 - V_1)}{g} - \frac{f_{av} N G^2 V_{av}}{2gm}$$

where $P_1 - P_2 = p$ = pressure drop, lb./sq. ft.

f = friction factor

N = equivalent length of straight pipe, ft.

G = weight velocity, lb./sec./sq. ft.

V = sp. vol., cu. ft./lb.

m = hydraulic radius = diam. (ft.) divided by 4 for circular pipes

Starting with the oil entering the convection section, the velocity at the end of this section was assumed to be 12.85 feet per second. Run 31 (Table II) shows that the specific volume is not changing rapidly with time. By interpolation a value of 0.0245 cubic foot per pound was selected for the 715° F. temperature. Since the specific volume at 570° F. was 0.022, according to the corrected specific gravity of 0.72 at that temperature, very little vaporization had evidently taken place at 730° F. and 300 pounds per square inch; hence, no correction was made for pressure. In a similar manner the pressure drops were calculated for consecutive sections of the furnace. Two trials were made in arriving at a consistent pressure drop for the tube section 135 to 150. The effective heating times are shown in Table III and also the calculation of the pressure drops. The doubling of the rate for a temperature rise of 22° F. was taken as an average temperature coefficient. The total calculated pressure drop falls only 12 pounds short of the actual drop of 430 pounds per square inch.

CRACKING TIME IN REACTION CHAMBER. To determine the length of time the charge was in the reaction chamber, the trial-and-error method had to be used. It was assumed as a first approximation that the cracking time in the reaction chamber was 9.5 minutes. The specific volume of the entering charge as calculated in the analysis of the pipe still operation was 0.15 cubic foot per pound, which is soon reduced to about 0.145 on account of the fall in temperature from 940° to 895° F.

According to run 38, Table II, the specific volume after 15.81 minutes total time, or 15.81 minus 6.40 = 9.40 minutes at 600 pounds per square inch and 903° F. in the reaction chamber would be 0.1420 cubic foot per pound. According to the data of runs 38 and 40, the density varies directly with pressure between 300 and 600 pounds per square inch gage, after 10 to 15 minutes cracking time at 894° F.; therefore the

DROP THROUGH PIPE STILL^a

$Z_{av.}$	$D_u/Z_{av.}$	$f_{av.}$	G^2/g	V_1	V_2	$V_2 - V_1$	$V_{av.}$	$G^2/2gm$	$\frac{G^2(V_2 - V_1)}{g}$	$\frac{f_{av.}NG^2V_{av.}}{2gm}$	Pressure $\frac{Lb./sq.}{ft.}$	Drop $\frac{Lb./sq.}{in.}$	Equivalent Cracking Time at 894° F. Min.
0.19	10350	0.0036	8530	0.0223	0.0245	0.0022	0.0234	55000	18.75	10200	10218	71.00	0.0024
0.14	14150	0.0035	8530	0.0245	0.0290	0.0045	0.0267	55000	38.40	9140	9178	63.80	0.0476
0.115	17250	0.0035	8530	0.0290	0.035	0.006	0.032	55000	51.10	6560	6611	45.80	0.50
0.11	19100	0.0037	7470	0.035	0.040	0.005	0.0375	44750	37.3	6230	6267.3	43.5	2.45
0.12	17350	0.0042	7660	0.040	0.048	0.008	0.044	46500	61.3	6030	6091.3	...	...
0.125	13950	0.0065	7660	0.040	0.090	0.050	0.065	46500	383	13420	13803	96.0	2.50
0.14	11100	0.0074	7850	0.090	0.150	0.06	0.105	48300	471	13700	14171	98.3	0.90
												418.4	6.40

Actual pressure drop = 430 lb./sq. in.

material leaving the chamber is $(0.1420/1) \times (614/414) = 0.210$ cubic foot per pound.

The average specific volume would be $(0.145 - 0.210)/2 = 0.1775$ cubic foot per pound.

The volume of the charge passing through the chamber in 9.5 minutes time would be $40.12 \times 9.5 \times 60 \times 0.1775 = 4045$ cubic feet.

The volume of the chamber, allowing for an average thickness of 3 inches of coke on the walls, was $4.5 \times 4.5 \times 3.14 \times 40 = 2550$ cubic feet; $(2550/4045) \times 9.5 = 6.00$ minutes in reaction chamber.

From the second and third successive approximations it was found that the time would be approximately 6.4 minutes in the reaction chamber, which gave a total cracking time of 12.80 minutes, including the cracking time in the furnace.

GASOLINE PRODUCTION. The plant was making 75.70 per cent by volume of gasoline based on the virgin gas oil, or $75.70/4 = 18.90$ per cent based on the combined feed.

Figure 3 shows that the laboratory data indicate a yield of 18.60 per cent gasoline of a similar nature from the same combined feed for the same equivalent time-temperature factor.

GAS YIELDS. The plant produced 720 cubic feet of dry gas per barrel of virgin oil or 180 cubic feet per barrel of combined feed, or $180/(42 \times 7.5) = 0.57$ cubic foot per pound of combined feed. The weight of 0.57 cubic foot of gas having a specific gravity of 1.0 at 60° F. and 14.4 pounds per square inch pressure is:

$$0.57 \times \frac{29}{359} \times \frac{492}{520} \times \frac{14.4}{14.7} = 0.043 \text{ lb. or } 4.3\% \text{ by weight of gas}$$

Laboratory results indicate about 6 per cent by weight of gas. The yield of gas by weight plus gasoline by volume in the plant equaled 22.90 per cent, while the laboratory gave 24.60 per cent for the same products.

Coke and Polymers

The plant data show a coke yield of 0.23 per cent coke and a residuum of 11.60 per cent by volume or $(1.025/0.9) \times 11.60 = 13.25$ per cent by weight, since the residuum had a specific gravity of 1.025 and the combined feed equaled 0.9 specific gravity.

The total of polymers and coke was 13.48 per cent by weight of the virgin oil, or 3.35 per cent on the basis of the combined feed.

According to the 894° F. line on Figure 6, the percentage of total polymers and coke equals 4 per cent for 12.90 minutes, indicating good agreement between plant and laboratory.

To determine the cracking time in the flash chamber calls for certain simplifying assumptions, since the composition of the vapor is changed as the result of the separation of the residuum. Furthermore, the laboratory apparatus had been designed to operate only under conditions comparable to those existing in a reaction chamber. Since 13.48 per cent by

weight of the charge was separated as residuum, $0.8652 \times 40.12 = 34.80$ pounds of vapor were formed in the flash chamber per second. Neglecting the change in composition and assuming that the volume of vapors may be estimated from data obtained at higher pressure, the specific volume of the vapor in the flash chamber may be taken as 0.685 cubic foot as compared with 0.188 cubic foot per pound in the reaction chamber:

$$0.188 \times \frac{1180}{1355} \times \frac{414}{99} = 0.685 \text{ cu. ft./lb.}$$

The volume of the flash chamber is 1140 cubic feet. Assuming that 50 seconds elapsed time in the flash chamber:

$$34.80 \times 50 \times 0.685 = 1190 \text{ cu. ft.}$$

$$\frac{1140}{1190} \times 50 = 48 \text{ sec. elapsed time}$$

A second approximation would give between 48 and 50 seconds time in the reaction chamber. Since the cracking rate doubles for every 22° F., the effective time at 894° F. in the reaction chamber is about 0.1 second. Therefore no appreciable cracking occurs beyond the reaction chamber.

Acknowledgment

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